Temperature Dependence of Photoisomerization. V. The Effect of Substituents on the Photoisomerization of Stilbenes and Azobenzenes

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Abstract: The results of a systematic investigation of the effect of substituents on the course of the direct *cis* $\rightleftharpoons$ *trans* photoisomerization of stilbene indicate that the isomerization follows the formation of triplet states, in agreement with the conclusions reached in parts IV and VI of this series. Intersystem crossing is furthermore identified in most cases as a $S_1 \rightarrow T_2$ process. The substituted stilbenes investigated now could be classified into five groups, according to the way in which the quantum yield ϕ_t of the *trans* → *cis* photoisomerization depends on the solvent and the temperature, in low-viscosity solvents. Group I consists of stilbene and its derivatives with substituents on the rings producing only limited spin-orbit coupling (*e.g.*, 4-methoxy, 4-dimethylamino, 4-chloro, and 4-fluoro). In these compounds ϕ_t decreases with decreasing temperature, corresponding to an activation energy of 1–4 kcal/mole. At the same time the quantum yield of the fluorescence of the *trans* isomer, ϕ_t, increases with decreasing temperature. The kinetic analysis indicates that fluorescence competes directly with isomerization (and intersystem crossing). Group II contains stilbene substituted at the rings with groups producing considerable spin–orbit coupling (*e.g.*, 4-bromo, 4-nitro, 4-aceto, 4-benzoyl, and 4-phenacyl). In these compounds ϕ_t is independent of the temperature, and we conclude that no energy barrier is necessary for intersystem crossing. Several explanations of this effect are advanced. In this group only 4-bromostilbene has a considerable (temperature-dependent) ϕ_F. Group III includes derivatives with donor–acceptor pairs at the 4 and 4′ positions. These compounds show strong dependence of ϕ_t on the polarity of the solvent. For 4-methoxy-4′-nitrostilbene in nonpolar solvents, ϕ_t is temperature independent, as in compounds in group II, while in alcoholic solvents it decreases on cooling, as observed with compounds in group I. 4-Dimethylamino-4′-nitrostilbene shows a very strong dependence of ϕ_t on the polarity and polarizability of the solvent, probably resulting from the very high dipole moments of this molecule in its excited states. Polar solvents tend to cause preferential stabilization of the excited *trans* isomer, and thereby reduce ϕ_t to practically zero. In hydrocarbon solvents ϕ_t of this compound decreases strongly with decreasing temperature. Group IV consists of stilbenes in which steric hindrance has been introduced by methylation at the central double bond or at the *ortho* ring positions. In these compounds ϕ_t is practically temperature independent. This behavior is the result of an increase in the energy of the S_1 state ^1B (through steric hindrance) relative to the energy of the T_2 state ^3H. In the latter the excitation is largely localized on the rings, and thus it is little influenced by steric hindrance. Group V contains α,β-difluoro- and dichlorostilbene. In these compounds ϕ_t is independent of the temperature. This contrasts with the behavior of the stilbenes halogenated in the *para* position and is ascribed to an enhanced efficiency of halogen atoms in spin-orbit coupling, when in the α and β positions. The quantum yield of the *cis*-to-*trans* photoisomerization (ϕ_c) of all the stilbenes investigated changes neither with the solvent nor with the temperature. In azobenzene derivatives no significant effect of the type of substituent on the temperature or solvent dependence of ϕ_t or ϕ_c was observed. All derivatives examined showed the photochemical behavior found for azobenzene proper (parts I and II). Thus the photoisomerization of azobenzenes probably proceeds *via* a different mechanism, such as a pyramidal inversion of a nitrogen atom, in contrast to stilbenes where rotation about the central double bond is required. The energy of activation for the thermal *cis* → *trans* conversion of hexamethylazobenzene was found to be identical with that found in azobenzene. This provides additional evidence for an inversion mechanism of *thermal* isomerization in azobenzene.

The photochemical behavior of stilbene may be changed by the introduction of substituents, which affect various properties of the molecule to a variable extent. Among these properties we can list the geometry of the π-electron cloud, the electron densities at the different positions, the intersystem (singlet → triplet) crossing probability, the availability of localized low-energy transitions (such as the $n-\pi^*$ transition), and changes in the separation between the levels brought about by the twisting around certain bonds.

It is not always possible to ascribe conclusively the effect of every kind of substitution to only one of these factors. In a few cases two factors enhance or oppose each other.

The effects of substitution on the course of the *cis* $\rightleftharpoons$ *trans* photoisomerization of stilbenes were examined in the present work. The information thus obtained complements studies of the effects, on this reaction, of viscosity, of perdeuteration, and of a heavy-atom solvent.[2,3] These studies represent different experimental approaches in the investigation of the mechanism of the *cis–trans* photoisomerization of stilbenes.

Photoisomerization quantum yields (ϕ_t, *trans* to *cis;* ϕ_c, *cis* to *trans*) and the quantum yield of fluorescence of the *trans* isomer (ϕ_F) were measured as functions of the temperature, as described in the previous investigations on this subject.[4–7] As a result of our

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(1) (a) Based on a part of the Ph.D. thesis submitted by D. Gegiou to the Weizmann Institute of Science, 1967; (b) to whom correspondence should be addressed.

(2) Part VI: D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 12 (1968).

(3) Part IV: K. A. Muszkat, D. Gegiou, and E. Fischer, *ibid.*, **89**, 4814 (1967).

(4) Part I: E. Fischer, *ibid.*, **82**, 3249 (1960).

(5) Part II: S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

(6) Part III: S. Malkin and E. Fischer, *ibid.*, **68**, 1153 (1964).

(7) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

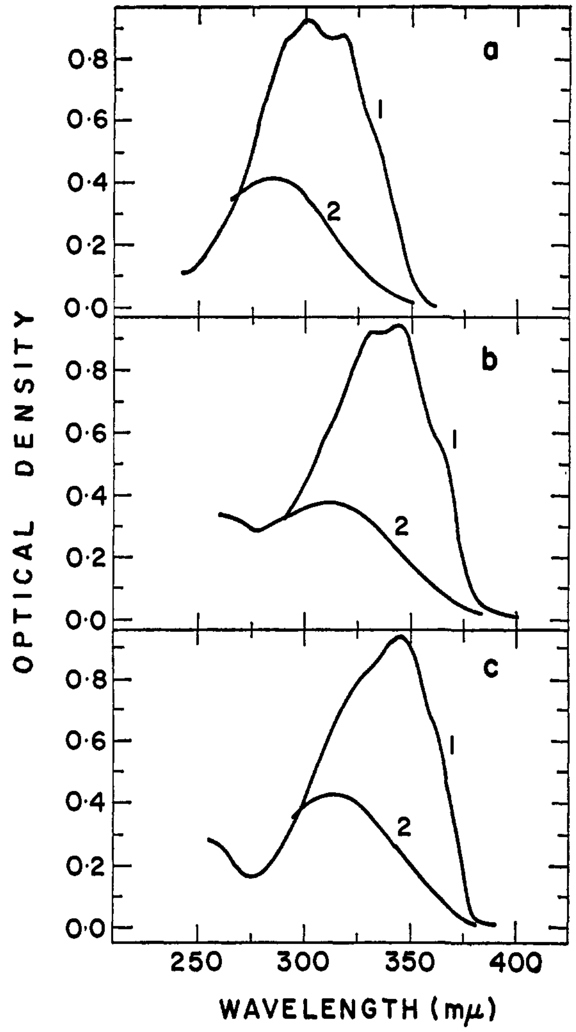

Figure 1. Absorption spectra of solutions in MCH–IH, measured in 10-mm cells at 25°: (a) 4-methoxystilbene, 3.15 × 10^{-5} *M;* (b) 4-nitrostilbene, 2.9 × 10^{-5} *M;* (c) 4-dimethylaminostilbene, 2.9 × 10^{-5} *M.* Curves 1, spectra of *trans* isomers; curves 2, extrapolated spectra of *cis* isomers.

recent work,[2] precautions were taken to ensure well-defined viscosity conditions.

The results described in this paper refer to low-viscosity media. In high-viscosity media, ϕ_t of sterically unhindered stilbenes drops considerably with increasing viscosity.[2]

The substituents investigated in the present study belong to five types, grouped according to their spectroscopic and photochemical effects: (I) substituents with a weak effect on intersystem crossing efficiency, (II) substituents with a strong effect on intersystem-crossing efficiency, (III) donor–acceptor substituent pairs, (IV) substituents exerting a strong steric hindrance to rotation about the 1-α bonds, and (V) substituents on the α positions.

The effects of the first four types of substituents on the photoisomerization of azobenzene were also investigated.

Results

I. Stilbene, and Stilbenes Substituted at the Rings with Groups Not Affecting the Singlet–Triplet Intersystem-Crossing Efficiencies. The photoisomerization of three compounds in this group (stilbene, 4-fluorostilbene, and 4-chlorostilbene) was investigated by Dyck and McClure.[7] In part III of the present series,[6] a similar but more quantitative study of stilbene and of 4-chlorostilbene (*inter alia*) was reported. The ϕ_t values of compounds in this group (measured in fluid hydrocarbon mixtures) were found to drop from about 0.3–0.5 at +25° to about zero at −180°, while ϕ_c is practically constant at least down to −160°. ϕ_F increases continuously from about 0.05 at 25° to somewhat less than unity at −180°. This type of behavior was now observed also in 4-methoxy- and 4-dimethylaminostilbene. The spectra of these compounds are given in Figure 1, while the quantum yields are listed in Table I. The hydrocarbon mixtures used were methylcyclohexane (MCH)–isohexane (IH), 2:1 by volume, which becomes "viscous" ($\eta > 10^4$ P) below −170°, and MCH–isopentane (IP), 1:4 by volume, which retains[8] its low viscosity down to about −185°.

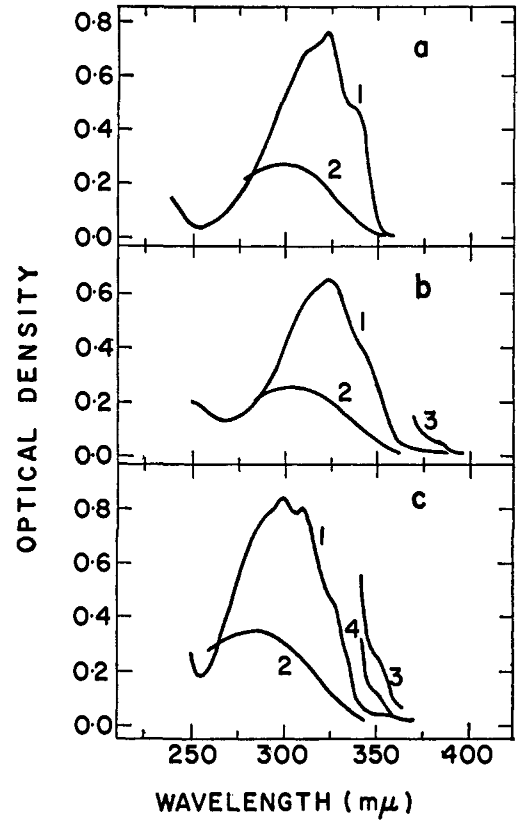

Figure 2. Absorption spectra of solutions in MCH–IH, measured in 10-mm cells at 25°: (a) 4-acetostilbene, 2.0 × 10^{-5} *M* (curve 1, *trans* isomer; curve 2, extrapolated spectrum of *cis* isomer); (b) 4-benzoylstilbene (curve 1, *trans* isomer; curve 2, extrapolated spectrum of *cis* isomer, both 1.7 × 10^{-5} *M;* curve 3, *trans* isomer, 1.7 × 10^{-4} *M*); (c) 4-phenacylstilbene (curve 1, *trans* isomer; curve 2, extrapolated spectrum of *cis* isomer, both 2.7 × 10^{-5} *M;* curve 3, *trans* isomer; curve 4, extrapolated spectrum of *cis* isomer, both 4.3 × 10^{-4} *M*).

II. Stilbenes Substituted at the 4 Position with Groups Enhancing the Intersystem-Crossing Efficiency. To this group belong stilbenes with the following substituents: bromo, nitro, aceto (CH_3CO–), benzoyl (C_6H_5CO–), and phenacyl ($C_6H_5COCH_2$–).[9]

The photochemistry of 4-bromostilbene has been described previously.[6,7] In these compounds, ϕ_t is

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[8] H. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

[9] We are indebted to Dr. H. Güsten, Karlsruhe, for synthesizing this compound and providing us with a sample.

Table I. Quantum Yields of Photoisomerization and of Fluorescence (*trans* Isomers) of Stilbenes (Group I) at Several Temperatures in Fluid Media

Stilbene in MCH–IH, 313-mμ Light[6]

t, °C	+25	−40	−65	−90	−105	−123	−140	−183[a]
ϕ_t	0.50	0.46	0.31	0.18	0.12	0.07	0.04	0.006
ϕ_c	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.12
ϕ_F[b]	0.06	0.14	...	(0.35)[c]	0.55	...	0.73	0.75

Stilbene in MCH–IH, Mole Fraction of *trans* Isomer, X_t, at Photoequilibrium

t, °C	+25	−60	−74	−100	−120	−140	−150	−180
X_t	0.07	0.12	0.15	0.27	0.45	0.65	0.88	0.90

Stilbene in Ethanol–Methanol (4:1), 313-mμ Light[2]

t, °C	+25	−100	−180[a]
ϕ_t	0.50	0.12	0.005
ϕ_c	0.35	0.35	0.20

Stilbene in Ethanol (305 mμ)[2]

ϕ_F	0.35[c]

4-Chlorostilbene in MCH–IH, 313-mμ Light[6]

t, °C	+25	−40	−80	−100	−140	−174[a]
ϕ_t	0.60	0.45	0.29	0.20	0.13	0.01
ϕ_c	0.42	0.42	0.50	0.50	0.50	0.1
ϕ_F[d]	0.08	0.29	0.46	0.50	0.52	0.52

4-Methoxystilbene in MCH–IP, 313-mμ Light[e]

t, °C	+25	−75	−120
ϕ_t	0.46	0.19	0.10
ϕ_c	0.25	...	0.34
ϕ_F	0.03	0.25	0.62
ϵ_t[f]	26,500	31,300	30,400
ϵ_c	6,100	9,100	11,300
X_t	0.11	0.15	0.56
X_t	0.10	0.15	0.45 (in MCH–IH)

4-Dimethylaminostilbene in Ethanol–Methanol (4:1), 365-mμ Light

t, °C	+25	−120
X_t	0.14	0.70

4-Dimethylaminostilbene in MCH–IH, 365-mμ Light

t, °C	+25	−75	−100	−120	−140
X_t	0.15	0.40	0.70	0.88	0.95

4-Dimethylaminostilbene in MCH–IP, 365-mμ Light

t, °C	+25	−70	−120
ϕ_t	0.52	0.1	0.006
ϕ_c	0.22	...	0.33
ϕ_F	0.05	0.21	0.22
ϵ_t	18,500	30,200	36,000
ϵ_c	3,000	5,200	8,000
X_t	0.06	0.27	0.93

4-Dimethylaminostilbene in Ethanol–Methanol (4:1), Excited at 330 mμ

t, °C	+25	−40	−75	−100	−130	−160
ϕ_F	0.04	0.18	0.40	0.53	0.59	0.70

[a] At these temperatures the viscosity of the solutions is high. [b] The original values[6] were normalized to $\phi_F = 0.75$ at −183°. This value was determined in the present study. [c] At −80°. [d] The original values were normalized to the above value for ϕ_F of *trans*-stilbene at −183°. [e] This compound in its *trans* form, in aliphatic hydrocarbons, tends to undergo profound spectral changes during irradiation at low temperatures. These changes revert on heating and are probably due to aggregation. Photostationary states at such low temperatures were therefore approached from a starting mixture rich in *cis*, which is much more soluble. [f] ϵ is the molar extinction coefficient.

almost constant from +25° to −180° as long as the viscosity of the medium is low. ϕ_c is also independent on the temperature. ϕ_F is very low and only in *trans*-4-bromostilbene is a sizable part of the excitation energy emitted as fluorescence at −180°. The spectra of some of these compounds are given in Figures 1 and 2, and the observed quantum yields are summarized in Table II. The drop in ϕ_t observed[6] for 4-bromostilbene in MCH–IH below −160° is an effect of the viscosity and does not occur in the more fluid MCH–IP mixture.

Table II. Quantum Yields of Photoisomerization and of Fluorescence (*trans* Isomer) of Stilbenes (Group II) at Several Temperatures in Fluid Media

4-Bromostilbene in MCH–IH, 313-mμ Light[6]

t, °C	+25	−40	−115	−135	−155	−183	−183[a]
ϕ_t	0.35	0.35	0.35	0.35	0.35	0.003	0.35
ϕ_c	0.16	0.16	0.16	0.16	0.19	0.05	0.16
ϕ_F	0.065	0.08	0.11	0.12	0.12	0.17	...

4-Nitrostilbene in MCH–IH, 365-mμ Light

t, °C	+25	−150	−180
ϕ_t	0.15	0.15	...
ϕ_c	0.20	0.20	...
ϕ_F	...	...	<0.01 (but observable)
X_t	0.13	0.13	...

4-Nitrostilbene in Ethanol–Methanol (4:1), 365-mμ Light

t, °C	+25	−150
X_t	0.13	0.13

4-Acetostilbene in MCH–IH, 313-mμ Light

t, °C	+25	−150
ϕ_t	0.5	0.5
ϕ_c	0.3	0.3

4-Benzoylstilbene in MCH–IH, 313-mμ Light

t, °C	+23	−150	−160	−165	−170	−180
ϕ_t	0.54	0.52	0.31	0.15	0.09	0.02
ϕ_c	0.27	0.27	0.21	0.14	0.13	0.11

4-Phenacylstilbene in MCH–IH, 313-mμ Light

t, °C	+25	−150
ϕ_t	0.5	0.5
ϕ_c	0.3	0.3

[a] In MCH–IP.

trans-4-Phenacylstilbene is nonfluorescent, even at −180°. ϕ_F of *trans*-4-acetostilbene in ethanol–methanol (4:1) is 0.03 at −180°, while for *trans*-4-benzoylstilbene in MCH–IH at −180° ϕ_F is less than 0.01. The drop in the ϕ_t value of benzoylstilbene below −150° in MCH–IH is similar to that observed in bromostilbene and thus is probably due to a high-viscosity effect.[2] Distinct n–π* transitions are seen in the absorption spectra of 4-benzoyl- and 4-phenacylstilbene (Figure 2). These bands undergo the characteristic blue shift in ethanol.[10] However, in both compounds irradiation at 365 mμ (*i.e.*, at the n–π* band) has the same results as irradiation at 313 mμ (at the π–π* band).

The solubility of the *trans* isomers of all three "keto" compounds in aliphatic hydrocarbons is very low. At concentrations above 10^{-4} *M* cooling of the solutions to below about −120° results in precipitation. Under the same conditions the absorption spectra of 10^{-5} *M* solutions of *trans*-4-aceto- and -4-benzoylstilbene gradually change, as shown in Figure 3. Eventually precipitation occurs even at this low concentration. When the solution is cooled quickly, to −180°, an intermediate stage preceding precipitation (which does not occur at −180°) is frozen in. In order to get the absorption spectrum of the real (*i.e.*, nonaggregated) *trans* isomer at −180°, we used the facts that the *cis* isomer is more soluble, that the photostationary state at −180° contains about 95% *trans* isomer, and that no aggregation takes place at −180° in a rigid glass.

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(10) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

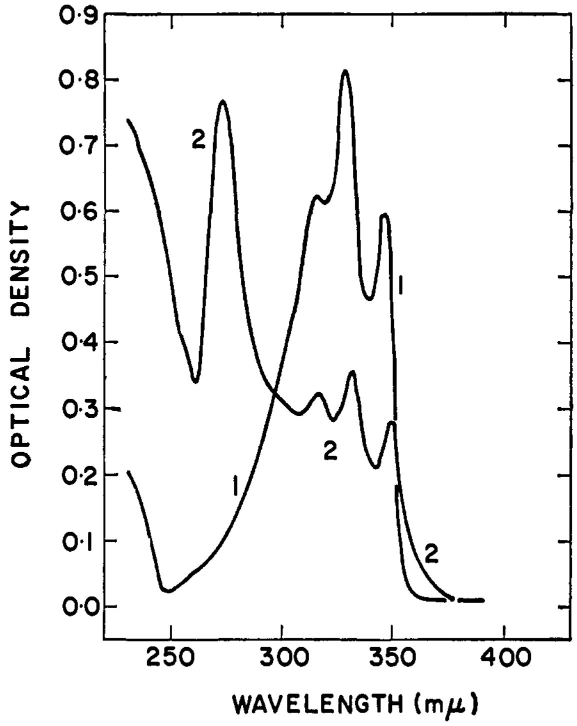

Figure 3. Absorption spectra of *trans*-4-acetostilbene, 1.0 × 10^{-5} *M* in MCH–IH, optical path 10 mm: curve 1, result of irradiation of *cis* isomer at −180°, causing practically complete conversion into *trans;* curve 2, original solution cooled gradually down to −180° (this curve represents an intermediate stage during aggregation, preceding precipitation).

Thus, by cooling *cis*-4-acetostilbene to −180° and then irradiating, we got the required spectrum. Somewhat similar results were obtained with 4-methoxystilbene described above. 4,4′-Dinitrostilbene probably belongs to this group. ϕ_t and ϕ_c for this compound have been reported[11] as 0.27 and 0.33, respectively, at room temperature; *i.e.*, they have values similar to those now observed for other compounds of this group.

III. Stilbene Disubstituted with Electron Donor and Acceptor Groups at the 4 and 4′ Positions. Schulte-Frohlinde, Blume, and Güsten have investigated the photoisomerization of 4-methoxy-4′-nitrostilbene and of 4-dimethylamino-4′-nitrostilbene in several solvents of different polarity, at room temperature.[11] They found that ϕ_t drops sharply with increasing polarity of the solvent while ϕ_c is not dependent on this factor. Thus, for the second compound ϕ_t in cyclohexane is 0.20 while in ethanol no *trans* → *cis* isomerization is observed.

The combined effect of the donor and of the acceptor substituents increases to a considerable extent the polarity of the molecule in the ground and even more so in the various excited states. Therefore strong solvent-dependent solvent–solute interactions are expected to determine the energy and nature of the molecule, both in the ground state and in the excited states.[12a] A similar situation has been observed also in 4-dimethylaminocinnamonitrile.[12b]

In the present work we have studied the temperature dependence of the photoisomerization of 4-methoxy-4′-nitrostilbene and of 4-dimethylamino-4′-nitrostilbene. The absorption spectra of these compounds in the two isomeric forms are given in Figure 4, while Table III summarizes the quantum yields at various temperatures. The absorption peaks in alcoholic solvents are shifted to longer wavelengths by 5 and 20 mμ, respectively.

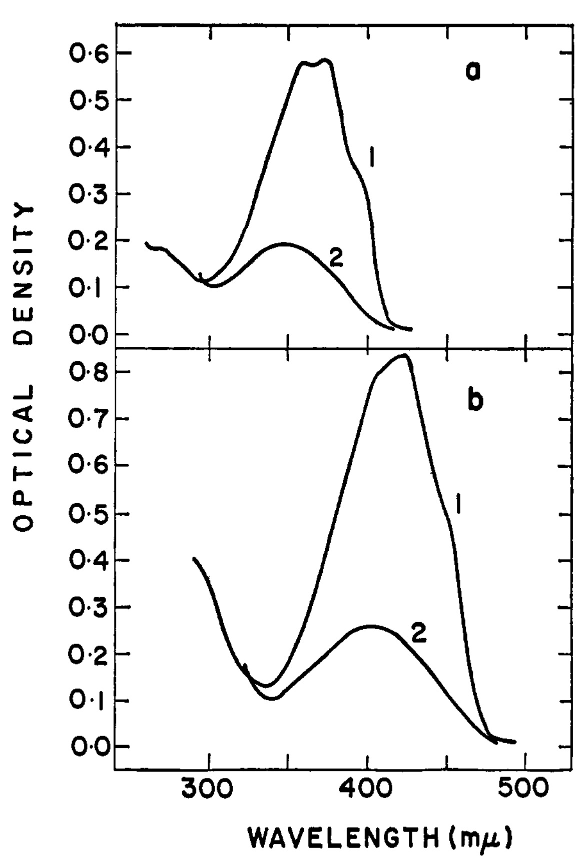

Figure 4. Absorption spectra of solutions in MCH–IH at 25°, 10-mm cells: (a) 4-methoxy-4′-nitrostilbene (1.85 × 10^{-5} *M*); (b) 4-dimethylamino-4′-nitrostilbene (2.55 × 10^{-5} *M*). Curves 1, *trans* isomer, curves 2, *cis* isomer (extrapolated).

Table III. Quantum Yields of Photoisomerization of Stilbenes (Group III) at Several Temperatures in Fluid Media

4-Methoxy-4′-nitrostilbene in MCH–Decalin (1:1), 313-mμ Light					
t, °C	+25	−100	−156		
ϕ_t	0.60	0.55	0.03		
ϕ_c	0.38	0.37	0.37		
405-mμ Light					
t, °C	+23	−100	−150	−156	−185
ϕ_t	0.70	0.60	0.25	0.03	0.008
ϕ_c	0.39	0.40	0.46	0.45	0.48
4-Methoxy-4′-nitrostilbene in Ethanol–Methanol (4:1), 405-mμ Light					
t, °C	+60	+23	−25	−75	−120
ϕ_t	0.10	0.10	0.06	0.04	0.02
ϕ_c	0.39	0.39	0.41	0.43	0.48
4-Dimethylamino-4′-nitrostilbene in MCH–Decalin (1:1), 436-mμ Light					
t, °C	+100	+50	+25	−25	−50
ϕ_t	0.37	0.31	0.22	0.06	0.015
ϕ_c	0.35	0.42	0.45	0.45	0.42
Toluene, 436-mμ Light					
t, °C	+100	+80	+25	+10	
ϕ_t	0.38	0.27	0.04	0.02	
ϕ_c	0.52	0.51	0.55	0.55	

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[11] D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962).

[12] (a) E. Lippert, *Angew. Chem.*, 73, 695 (1961); (b) E. Lippert and W. Lüder, *J. Phys. Chem.*, **66**, 2430 (1962).

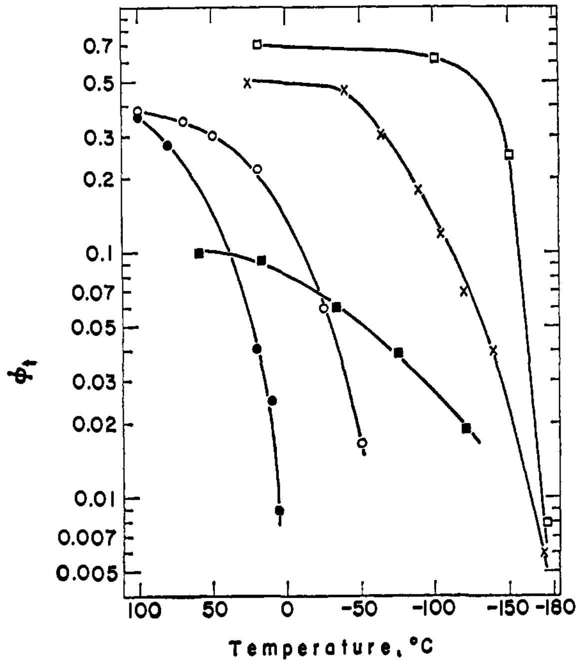


Figure 5. Plot of ϕ_t (logarithmic scale) *vs.* temperature (°C) for the following compounds: stilbene in MCH–IH (×); 4-methoxy-4′-nitrostilbene in MCH–decalin (□); same compound, in ethanol–methanol (■); 4-dimethylamino-4′-nitrostilbene, in MCH–decalin (○); same compound, in toluene (●).

The results show that, while ϕ_c does not change with temperature in both compounds and all solvents, ϕ_t of the first compound in hydrocarbon solvents changes with viscosity but not with temperature, while ϕ_t of the second compound decreases with decreasing temperature more sharply than in any other stilbene derivative examined so far. Figure 5 summarizes the temperature dependence of ϕ_t in both compounds, in comparison with that of stilbene. In alcoholic solutions of 4-nitro-4′-dimethylaminostilbene, no *trans* → *cis* photoconversion takes place at room temperature, *i.e.*, $\phi_t = 0$. Even in heptanol at 150° only about 4% of this compound is converted into the *cis* form in the photostationary state with light at 436 mμ. The above data also show the pronounced solvent dependence of ϕ_t.[11]

trans-4-Methoxy-4′-nitrostilbene in MCH–decalin has a fluorescence yield below 1% even at −170°, while in ethanol–methanol $\phi_F \approx 0.2$ at −180° (estimated by comparison with quinine sulfate). The emission of *trans*-4-dimethylamino-4′-nitrostilbene in MCH–IH shows considerable structure. Its yield is about 0.2 at room temperature and increases to 0.5 at −50°. At lower temperatures ϕ_F drops, probably because of aggregation followed by precipitation. In alcohol both compounds show a pronounced change of the emission spectrum with the temperature. Figure 6 shows the results. No parallel change of either the absorption or the excitation spectra was observed.

IV. Sterically Hindered Stilbenes. In this group of compounds the substituents either at the 2 and 6 ring atoms or at the α (or β) bridge atoms give rise to steric hindrance, which is relieved mainly by twisting to a variable extent around the 1-α bonds.[13] This causes both hypsochromic and hypochromic shifts of the long-wavelength transition ($^1B \rightarrow {}^1A$) of these compounds, as compared with the sterically unhindered and almost planar *trans*-stilbene. This is seen in Figure 7, where the absorption spectra of 2,4,6-trimethylstilbene (I) and 2,2′,4,4′,6,6′-hexamethylstilbene (II) are compared

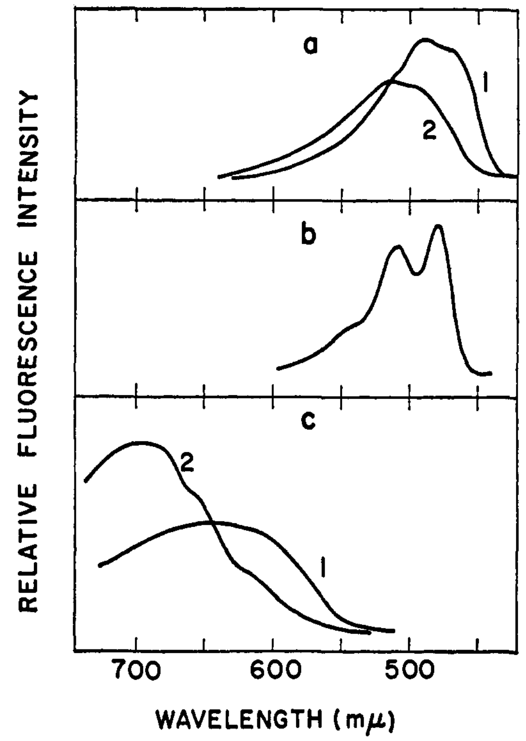
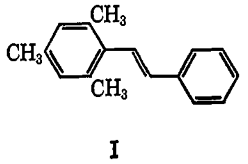


Figure 6. Emission spectra of the *trans* isomers of stilbene derivatives, excited at 400 mμ, 5 × 10^{-6} *M*: (a) 4-methoxy-4′-nitrostilbene in ethanol–methanol (curve 1 at −180°; curve 2 at −130°); (b) 4-dimethylamino-4′-nitrostilbene in MCH–IH at −50°; (c) 4-dimethylamino-4′-nitrostilbene in ethanol–methanol. Curve 1 at −180°; curve 2 at −130° (corrected spectra).



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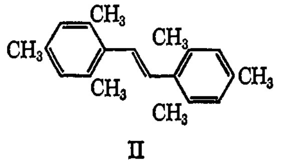

II

with those of the two isomers of stilbene. The spectra of the two hindered derivatives in their *trans* form are clearly similar to that of *cis*-stilbene, both regarding position and absence of vibrational structure. On cooling the solutions, the long-wavelength band in all three spectra undergoes a red shift and a pronounced increase in intensity.

We have investigated the photoisomerization of four stilbene derivatives in which steric effects prevail: 2,4,6-trimethylstilbene (I), 2,2′,4,4′,6,6′-hexamethylstilbene (II), α-methylstilbene (III), and α,β-dimethylstilbene (IV). The steric hindrance is moderate in I and in III, and strong in II and in IV.[14]

Experiments were carried out with 10^{-5}–10^{-2} *M* solutions in MCH–IH. The isomeric composition of the photostationary mixtures in solutions from 5 × 10^{-4} *M* upward was determined by vapor phase chromatography, which also served to check the spectrophotometric analysis applied at lower concentrations.

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(13) (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 15; (b) H. H. Jaffé and M. Orchin, *J. Chem. Soc.*, 1078 (1960).

(14) H. Suzuki, *Bull. Chem. Soc. Japan*, **33**, 396, 406 (1960).

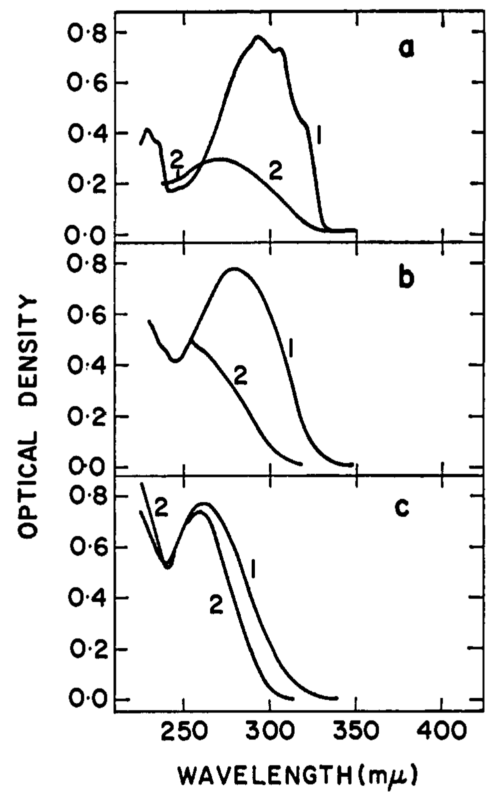

Figure 7. Absorption spectra of solutions in MCH–IH at 25°, 10-mm cells: (a) stilbene, 2.75 × 10^{-5} *M;* (b) 2,4,6-trimethylstilbene, 3.5 × 10^{-5} *M;* (c) 2.2′,4,4′,6,6′-hexamethylstilbene, 5.15 × 10^{-5} *M.* Curves 1 and 2 denote *trans* and *cis* isomers, respectively. Curves 2 in b and c were derived by extrapolation.

At 300 mμ the ratio $\epsilon_{trans}/\epsilon_{cis}$ was thus found to be 7.7 for I and 5.7 for II. Irradiation with light at 254 mμ at room temperature caused irreversible side reactions, and isomerization yields were therefore determined at this wavelength only at −180°.

The results obtained for all compounds except α,β-dimethylstilbene are listed in Table IV and show that ϕ_t is practically temperature independent.

The fluorescence spectra of trimethyl- and hexamethylstilbene at −180° are given in Figure 8 and show considerable structure, despite the lack of structure in the absorption spectra at −180° (Figure 7). This suggests that the equilibrium configuration in the excited state differs considerably from that in the ground state. The observed Stokes shift is indeed larger than in stilbene, though not exceptionally so. The yields ϕ_F are seen to decrease with increasing steric hindrance (at −180° ϕ_F = 0.75 for stilbene, 0.35 for trimethylstilbene, and 0.13 for hexamethylstilbene). For the sterically hindered *cis*-stilbene[6,15] ϕ_F = 0.05 at −160°. This may be due at least partly to the competing *cis* → *trans* photoconversion, which is not slowed down on cooling, as it is in *trans*-stilbene, where emission and photoconversion were seen to be the two major competing processes of energy dissipation.[6] The same holds for ϕ_t in the above two methylated compounds. Indeed, 1,2-diphenylcyclopentene which is sterically hindered just like *cis*-stilbene, but of course unable to

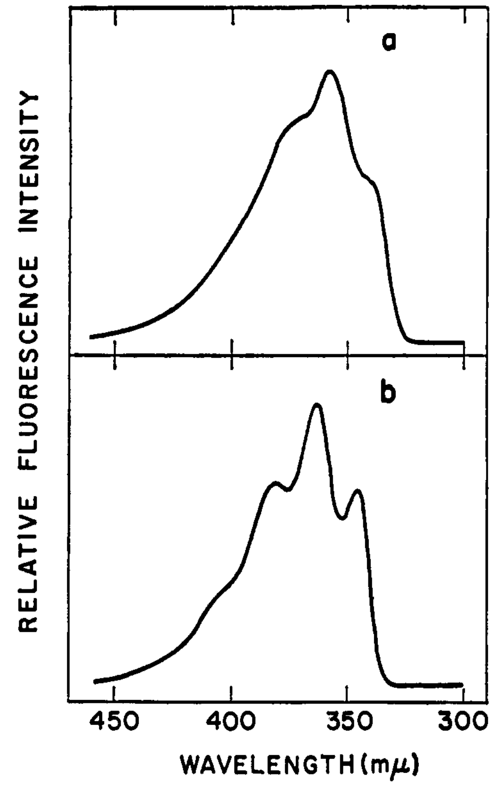

Figure 8. Emission spectra of the *trans* isomers of methylstilbenes (solutions in MCH–IH, measured at −180°, excited at 315 mμ); (a) trimethylstilbene, 1.7 × 10^{-5} *M;* (b) hexamethylstilbene, 2.5 × 10^{-5} *M.*

Table IV. Quantum Yields of Photoisomerization of Stilbenes (Group III) and of Fluorescence of the *trans* Isomers at Several Temperatures in Fluid Media

2,4,6-Trimethylstilbene in MCH–IH, 313 mμ-Light

t, °C	+25	−180
ϕ_t	0.47	0.13
ϕ_c	0.39	0.40
ϵ_t	8000	17,000
ϵ_c	800	1000
X_t	0.08	0.14

Excited at 315 mμ

t, °C	+25	−60	−100	−120	−140	−160	−180
ϕ_F	0.003	0.005	0.01	0.03	0.10	0.31	0.35

α-Methylstilbene, 313-mμ Light

Solvent	IH	MCH–IP	MCH–IH
t, °C	+25	−175	−187
ϕ_t	0.48	0.32	
ϕ_c	0.58	0.46	
ϕ_F	0.003	...	0.21
ϵ_t	2200	2000	
ϵ_c	1100	1000	
X_t	0.37	0.42	

2,2′,4,4′,6,6′-Hexamethylstilbene in MCH–IH

λ,[a] mμ	313	313	254
t, °C	+25	−180	−180
ϕ_t	0.48	0.52	0.51
ϕ_c	0.40	...	0.42
ϵ_t	1800	5400	11,000
ϵ_c	125	...	15,000
X_t	0.055	~0.01	0.55

Excited at 315 mμ

t, °C	+25	−60	−100	−120	−140	−160	−180
ϕ_F	<0.001	<0.001	0.001	0.008	0.08	0.11	0.13

[a] Irradiation wavelength.

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(15) (a) H. Stegemeyer, *J. Phys. Chem.,* **66,** 2486 (1962); (b) F. Aurich, M. Hauser, E. Lippert, and H. Stegemeyer, *Z. Physik. Chem.* (Frankfurt), **42,** 123 (1964); (c) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.,* **4,** 259 (1965).

isomerize, was found[16] to have $\phi_F = 0.43$ at −180°. However, in this molecule twisting along the α–β central bond is also impossible either in the ground or in any excited state, and therefore deactivation which involves this motion in *cis*-stilbene is inactive in this molecule.

α,β-Dimethylstilbene is not included in Table IV. Since in this compound no light is absorbed at 313 mμ by either isomer, irradiation had to be carried out at 254 mμ, which again causes some efficient photochemical side reaction. The isomeric composition could therefore be determined only by vapor phase chromatography. This method was applied to the photostationary mixtures obtained at +25 and −175° with light at 254 mμ. Together with the ε values at this wavelength[17] ($\epsilon_{trans} = \epsilon_{cis} = 8300$), this yields the following values for the ratios ϕ_t/ϕ_c: 0.7 + 25° and 0.25 at −175°. Moreover, the initial rates of *trans* → *cis* photoisomerization were found to be similar at +25° and at −175°. It may therefore be concluded that in this compound ϕ_t is only slightly dependent on temperature.

Finally, the photoisomerization of hexamethylstilbene was sensitized by benzophenone, by irradiating with light absorbed only by the latter, in a way similar to that described for stilbene proper.[6] Solutions 10^{-3} *M* in hexamethylstilbene and 5×10^{-4} in benzophenone were irradiated at 365 mμ. The photostationary state attained contained 38% *cis* isomer, indicating that here too the excited state from which isomerization occurs may be attained by energy transfer from triplet benzophenone.

V. **α-Substituted Stilbenes**. The photoisomerization of two sterically hindered α-substituted molecules, α-methylstilbene and α,β-dimethylstilbene, was described above. Two other cases of α substitution, α,β-difluorostilbene and α,β-dichlorostilbene, were studied in the present investigation.

Both from the value of the van der Waals radius of the fluorine atom (R_H = 1.2 Å, R_F = 1.35 Å)[18] and from the spectrum of *trans*-difluorostilbene (Figure 9) it is seen that this molecule is sterically unhindered. α,β-Dichlorostilbene is moderately hindered.[14,17] In both compounds a moderate drop in ϕ_t is observed (Table V) on lowering the temperature to −180°.

VI. **Azobenzene Derivatives**. As far as possible, substituents similar to those described in connection with stilbene were introduced in azobenzene. Derivatives investigated were 2,4,6-trimethyl and 2,2′,4,4′,6,6′-hexamethyl (analogous to group IV above), 4-nitro (group II), 4-nitro-4′-methoxy and 4-nitro-4′-dimethylamino (group III). None of these compounds fluoresces.

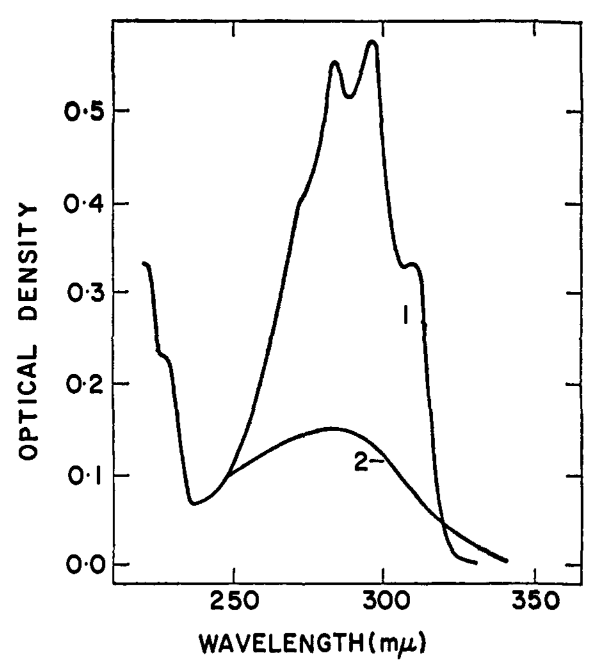

Figure 9. Absorption spectrum of α,β-difluorostilbene, 1.75×10^{-5} *M* in MCH–IH at +25°, 10-mm light path. Curve 1, *trans* isomer; curve 2, extrapolated spectrum of *cis* isomer.

Table V. Quantum Yields of Photoisomerization and of Fluorescence (*trans* Isomers) of α,β-Dihalogenostilbenes at Several Temperatures

α,β-Difluorostilbene, 313-mμ Light		
t, °C	+25	−183
Solvent	MCH–IH	MCH–IP
ϕ_t	0.35	0.20
ϕ_c	0.45	0.4
ϕ_F	<0.001	0.35[a]
ϵ_t	17,200	34,500
ϵ_c	3,200	6,400
χ_t	0.20	0.30
α,β-Dichlorostilbene in MCH–IP, 313 mμ Light		
t, °C	+25	−175
ϕ_t	0.41	0.08
ϕ_c	0.14	0.15
ϕ_F	<0.001	0.002
ϵ_t	1100	2900
ϵ_c	2800	7500
χ_t	0.47	0.83

[a] In MCH–IH.

The absorption spectra of the two sterically hindered derivatives are compared in Figure 10 with that of azobenzene. The sole effect of methylation in the positions *ortho* to the N=N bond is a slight bathochromic and hypochromic shift of the π–π* band (λ_{max} 315, 322, and 325 mμ, respectively), while the n–π* band is both shifted to longer wavelengths and higher intensities [λ_{max} 445 mμ (450), 460 mμ (750), 470 mμ (950)]. The situation regarding the π–π* band is thus radically different from that observed with the analogous stilbenes (Figure 7), indicating that steric effects, *i.e.*, impaired coplanarity in the *trans* isomers, are much less pronounced or less effective. Possibly twisting of a phenyl ring with respect to the N=N bond decreases resonance along the whole molecule, but at the same time increases the conjugation between this phenyl ring and the lone electron pair of one of the nitrogen atoms. This could also explain the fact that methylation increases the intensity of the n–π* band.[19]

The absorption spectra of 4-nitro- and 4-nitro-4′-methoxyazobenzene are shown in Figure 11. The substituent effect is again much smaller than in the stilbenes.

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(16) K. A. Muszkat and E. Fischer, *J. Chem. Soc., B*, 662 (1967).

(17) J. Derkosch and G. Friedrich, *Monatsh. Chem.*, **84**, 1146 (1953).

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(19) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 8.

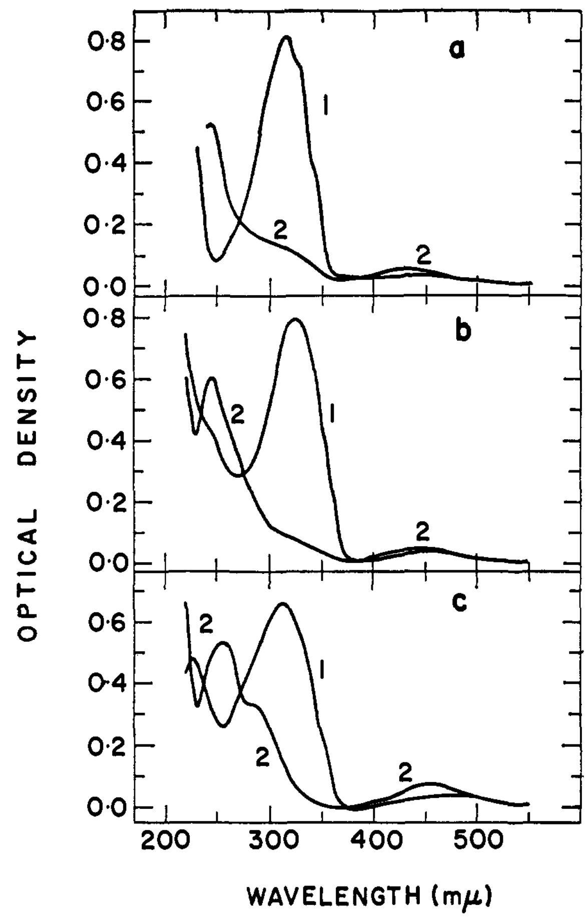

Figure 10. Absorption spectra of solutions of azobenzenes in MCH-IH at 25°, 10-mm cells: (a) azobenzene, 3.7 × 10^{-5} *M;* (b) 2,4,6-trimethylazobenzene, 4.25 × 10^{-5} *M;* (c) 2,2′,4,4′,6,6′-hexamethylazobenzene, 3.65 × 10^{-5} *M.* Curves 1 and 2 denote *trans* and *cis* isomers, respectively. Curves 2 in b and c are extrapolated.

Results regarding isomerization are summarized in Table VI and show that the regularities observed in the effect of substituents on the type of dependence of ϕ_t on temperature in stilbenes do not exist in azobenzene. All the substituted azobenzenes show a slight decrease of ϕ_t with decreasing temperature. ϕ_t values for irradiation at the n–π* band are in most cases larger than for irradiation at the π–π* transition, while ϕ_c values are independent both of temperature and of wavelength, and all fall within a narrow range, 0.45 ± 0.10. This type of behavior was previously observed in azobenzene,[4,5] for which the previously reported data are listed here too. ϕ_t's are generally smaller than 0.25 and decrease at lower temperatures to an extent which is in most cases similar in the two irradiation regions. No clear-cut effect of the exact energy of the absorbed quantum in the π–π* or n–π* bands is observed. A slight reduction of ϕ_t at high viscosity has been observed in azobenzene.[2]

Table VI. Quantum Yields of Photoisomerization of Azobenzenes in MCH-IH at Several Temperatures, with Light at Various Wavelengths

Azobenzene[5]

t, °C	+23		−140	
λ, mμ	313	436	313	436
ϕ_t	0.09	0.25	0.03	0.16
ϕ_c	0.40	0.40	0.45	0.55

2,4,6-Trimethylazobenzene

t, °C	+23			−180		
λ, mμ	285	313	510	285	313	510
ϕ_t	0.16	0.10	0.16	0.04	0.03	0.02
ϕ_c	0.37	0.35	0.38	0.45	0.4	0.33
ϵ_t	8500	17,000	390	8000	19,000	600
ϵ_c	5000	1300	190	6000	1500	90
X_t	0.60	0.17	0.50	0.90	0.50	0.75

2,2′,4,4′,6,6′-Hexamethylazobenzene

t, °C	+23				−140		−180		
λ, mμ	280	313	436	510	313	510	280	313	510
ϕ_t	0.13	0.09	0.16	0.2	0.06	0.09	0.06	0.03	0.02
ϕ_c	0.37	0.33	0.44	0.44	0.45	0.44	0.5	0.35	0.5
ϵ_t	7400	16,400	700	720	23,000	1300	10,700	24,500	1400
ϵ_c	8100	3100	1600	520	5650	450	8500	6200	430
X_t	0.75	0.40	0.87	0.60	0.65	0.64	0.92	0.75	0.90

4-Nitroazobenzene

t, °C	−30		−80		−130	
λ, mμ	313	436	313	436	313	436
ϕ_t	0.07	0.14	0.03	0.06	0.01	0.03
ϕ_c	0.38	0.36	0.37	0.40	0.35	0.35

4-Methoxy-4′-nitroazobenzene

t, °C	−30		−100		−150
λ, mμ	365	436	365	436	365
ϕ_t	0.10	0.17	0.07	0.09	0.03
ϕ_c	0.50	0.55	0.55	0.52	0.55

Table VII. Activation Energies, E_a, and First-Order Rate Constants, *k*, for the Thermal *cis*-to-*trans* Isomerization of Some Azobenzene Derivatives, in MCH Solutions

Substitution	E_a, kcal/mole	*k*, min^{-1} (*t*, °C)	Temp range, °C
2,4,6-Trimethyl	24	2.6 × 10^{-2} (75)	75–95
2,2′,4,4′,6,6′-Hexamethyl	24	1.5 × 10^{-2} (70)	70–97
4-Nitro	24	1.35 × 10^{-2} (45)	45–70
4-Methoxy-4′-nitro	23[a]	8.7 × 10^{-3} (25)	25–55

[a] Measured both in MCH and in 1-propanol–2-propanol (1:1).

The thermal *cis* → *trans* isomerization was also investigated for all the above compounds. With the exception of 4-nitro-4′-dimethylaminoazobenzene, first-order kinetics were observed throughout, with activation energies of 23–24 kcal/mole, which are practically identical with the value reported[20] for azobenzene proper (23 kcal/mole). 4-Nitro-4′-dimethylaminoazobenzene undergoes acid–base-catalyzed isomerization, making kinetic measurements unreliable. The results are listed in Table VII. The fact that the kinetics in hexamethylazobenzene are closely similar to those in azobenzene supports the view[21] that thermal isomerization in azobenzene proceeds by an inversion mechanism, rather than by twisting the central double bond. In the latter case the methyl groups in the *ortho* positions would be expected to hinder the thermal *cis* → *trans* conversion.

Discussion

The following discussion refers mainly to stilbene, about which more information[2,3] is available. The most satisfactory description of the photoisomerization process is afforded by the diagram shown in Figure 12. The steps proper to the *cis* molecule are denoted with a prime, radiative transitions by full lines,

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(20) R. J. W. Lefèvre and J. Northcott, *J. Chem. Soc.*, 867 (1953).

(21) E. R. Talaty and J. C. Fargo, *Chem. Commun.*, 65 (1967), and other references listed therein.

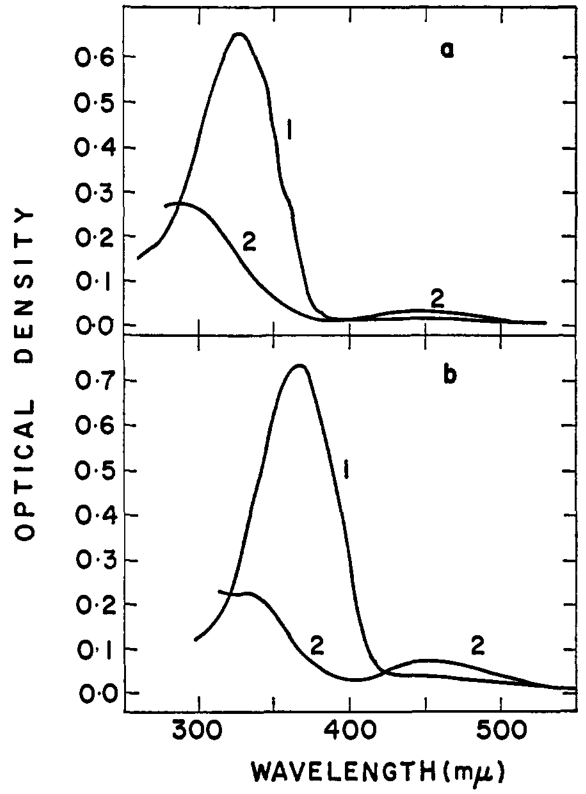

Figure 11. Absorption spectra of solutions in MCH–IH at 25°, 10-mm cells: (a) 4-nitroazobenzene, 1.85×10^{-5} *M*; (b) 4-methoxy-4′-nitroazobenzene, 2.3×10^{-5} *M*. Curves 1 and 2 denote the measured spectra of the *trans* isomers and the extrapolated spectra of the *cis* isomers, respectively.

and radiationless ones by broken lines. The present description differs from the previous one[2] in a few minor details, rendered necessary by recent theoretical results (see below).

Following excitation a to one of the singlet levels (S_1 or S_n), the molecule is eventually converted into the vibrationally relaxed first excited singlet level S_1. This level decays by three processes: fluorescence (F), internal conversion $S_1 \rightarrow S_0$ (b), and intersystem crossing to the triplet system (d). The latter probably takes place to the second triplet level, T_2, which is approximately isoenergetic with S_1. This is expected in view of the known preference for isoenergetic pathways of energy conversion.[22,23] T_2 decays to T_1 (step e), which relaxes into a twisted (90°?) state X (step f). The latter decays to the ground states, S_0 and S_0', of the two isomers (steps g and g′). Steps (f + g′) and (f′ + g) constitute the actual isomerization. Steps k and h might be of importance under certain conditions. Within the framework of this scheme, the temperature dependence of ϕ_t (group I) is due to a temperature dependence of step d, while the viscosity dependence[2] of ϕ_t is due to such a dependence of either step f, g′, or both. Under conditions of viscosity-inhibited isomerization (compounds of groups I and II in highly viscous media), the main pathways of energy dissipation from S_1^{trans} are thus $S_1 \rightarrow S_0$ (steps b and F), and

$$S_1 \xrightarrow{d} T_2 \xrightarrow{e} T_1 \xrightarrow{f} X \xrightarrow{g} S_0$$

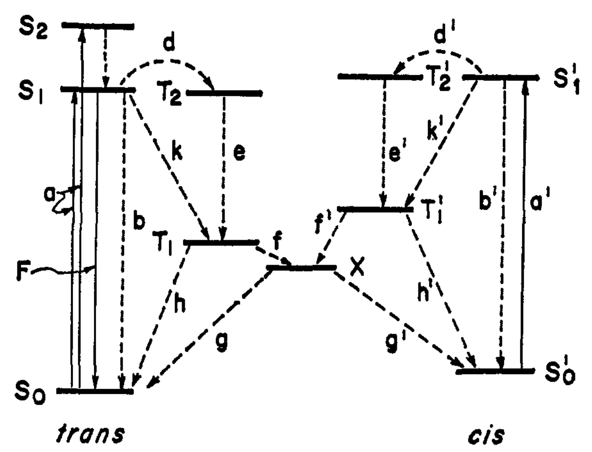

Figure 12. Schematic display of processes participating in the *cis–trans* photoisomerization of stilbenes.

The by-passing steps k and h might also participate. The relative importance of the various radiationless transitions is difficult to assess.

The basic assumption in the present discussion is that the direct photoisomerization proceeds through triplet level intermediates. This assumption is based[3] on the external enhancement of ϕ_t in stilbene at low temperatures, on the internal enhancement of ϕ_t (Table II, previous section), and on the uncoupling of fluorescence from the *trans*-to-*cis* isomerization in stilbene in highly viscous media.[2] The results of other experiments (*e.g.*, the identical photochemical behavior of normal and deuterated stilbene) which were thought to be opposed[24] to this assumption were later shown to be readily explained by it.[3] The mechanism depicted in Figure 12 has several features in common with previous schemes.[7,11,25,26]

Several of the steps suggested in Figure 12 are based on experimental results, on theoretical predictions, and on analogy with processes observed in other excited molecules. Step b, the $S_1 \rightarrow S_0$ internal conversion, probably exists to a varying extent in all *trans*-stilbenes. Thus, in *trans*-stilbene at −180° $\phi_t \approx 0$, because intersystem crossing, d, is frozen out, but ϕ_F is still only 0.75, so that the quantum yield of b is about 0.25 at this temperature. Additional information about this process is lacking; *i.e.*, it is not possible to decide whether it is constant or else temperature dependent and proportional to ϕ_F (at −180° $\phi_b = {}^1/_3\phi_F$).

A similar situation is encountered with all the other molecules of group I. Estimation of ϕ_{ISC} values by an independent method would make possible some progress about this subject.

4-Bromostilbene, which is the only molecule of group II with a considerable ϕ_F at low temperatures, and molecules of group IV such as hexamethyl- and trimethylstilbene present a different case. ϕ_t in these molecules is constant so there is good reason to believe that ϕ_{ISC} is also constant. ϕ_F changes, however, with the temperature, presumably because the quantum yield of step b increases with increasing temperature, as

$$\phi_b = 1 - \phi_{ISC} - \phi_F$$

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(22) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(23) J. N. Murrell, ref 19, Chapter 14.

(24) (a) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Am. Chem. Soc.*, **88** 2336 (1966); (b) J. Saltiel, *ibid.*, **89**, 1037 (1967).

(25) T. Förster, *Z. Elektrochem.*, **56**, 716 (1952).

(26) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

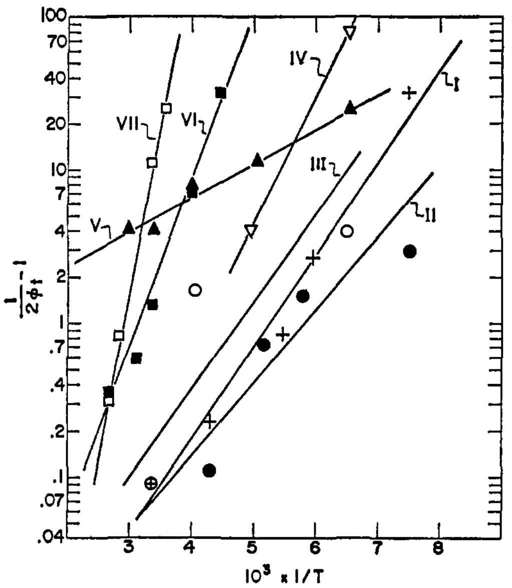


Figure 13. Semilogarithmic plot of $[(1/2\phi_t) - 1]$ *vs.* $1/T$. For stilbene only, semilogarithmic plot of $[(1/\phi_{ISC}) - 1]$ *vs.* $1/T$. I, stilbene in MCH–IH (+); II, 4-chlorostilbene in MCH–IH (●); III, methoxystilbene in MCH–IP (○); IV, 4-dimethylaminostilbene in MCH–IP (▽); V, 4-methoxy-4′-nitrostilbene in ethanol–methanol (▲); VI, 4-dimethylamino-4′-nitrostilbene in MCH–decalin (■); VII, same, in toluene (□).

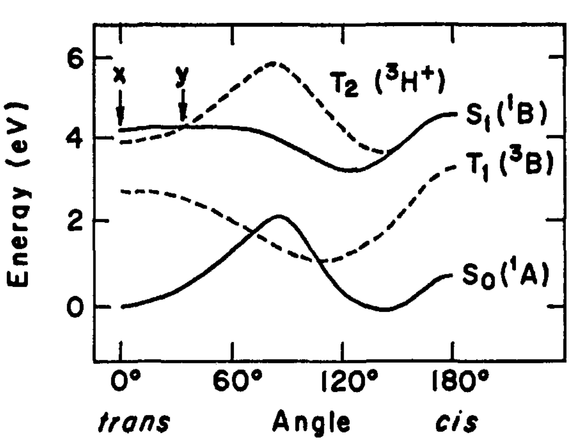


Figure 14. Dependence of energies of the ground state and of some excited states of stilbene on the angle of twist about the central double bond (modified, after Borrell and Greenwood[28]).

Table VIII. Activation Energies, E_a, for the *trans* → *cis* Photoisomerization of Stilbene and Its Derivatives

Compound	Solvent	E_a, kcal/mole
Stilbene[a]	MCH–IH	1.7
Stilbene[b]	MCH–IH	3.0
4-Chlorostilbene	MCH–IH	2.2
4-Methoxystilbene	MCH–IH	2
4-Dimethylaminostilbene	MCH–IH	3.8
4-Methoxy-4′-nitrostilbene	Ethanol–methanol	1
4-Dimethylamino-4′-nitrostilbene	MCH–D	5.5
	Toluene	11

[a] Taken from part III.[6] [b] Calculated from the temperature dependence of $1 - {}^4/_3\phi_F$; *cf.* text and part VI.[2]

Step b′ in *cis*-stilbene involves one chemical path of energy dissipation, namely photocyclization by a singlet level process to 4a,4b-dihydrophenanthrene with a quantum yield of 0.1–0.2 and an activation energy of about 3 kcal/mole.[16] This process involves a considerable fraction of the total excitation energy also in the *cis* isomers of 4-chloro- and 4-bromostilbenes and a much smaller fraction in hexamethyl-, 4-methoxy-, and 4-dimethylaminostilbenes, and does not take place in compounds of groups II (with the exception of 4-bromostilbene) and III.[16,27]

Regarding the temperature dependence of ϕ_t observed in the compounds of groups I and III, this may be expressed in terms of Arrhenius parameters for step d, provided we assume[6] that only this step is temperature dependent and follows an Arrhenius equation. As shown earlier,[6] these assumptions lead to a linear relationship between ln $[(\alpha/\phi_t) - 1]$ and T^{-1}, with the slope being equal to E_a/R. Here E_a is the activation energy, while α is the probability of decay of state X to S_0', $\alpha = k_{g'}/(k_g + k_{g'})$. It was found[6] to be approximately 0.5 in stilbene, and in the absence of other information we shall assume it to have a similar value in the other cases (groups I and III). Figure 13 shows the extent to which the linear relationship holds. The values of E_a calculated from the slopes of the curves are listed in Table VIII.

In the above development no use was made of the absolute values of the quantum yields, ϕ_{ISC}, of intersystem crossing ($S_1 \rightarrow T_2$, step d). As mentioned above, it would be desirable to have such values[2] and calculate E_a from their temperature dependence. A derivation similar to the previous one[6] leads to

$$\ln (\phi_{ISC}^{-1} - 1) = \text{constant} - E_a/RT \qquad (1)$$

If certain assumptions are made, ϕ_{ISC} can be estimated from the quantum yields either of the steps preceding intersystem crossing (*i.e.*, radiative and radiationless transitions $S_1 \rightarrow S_0$, steps F and b) or of the steps following such crossing (*i.e.*, steps h, f, and g′). In the first case we have $\phi_{ISC} = 1 - \phi_F - \phi_b$; *i.e.*, ϕ_b, the yield of the internal conversion, has to be estimated. If we assume[2] that ϕ_b is always a certain fraction of ϕ_F (*e.g.*, $^1/_3$, as observed in stilbene at −180°) and neglect step k, then the change of ($\phi_{ISC} = 1 - {}^4/_3\phi_F$) with temperature according to eq 1 yields the activation energy E_a for step d as before. In Figure 13, curve I, and in Table VIII we have applied this method to stilbene. In Table VIII the results obtained for stilbene by both methods are compared. The discrepancy found indicates that the above assumptions are not wholly justified.

In the second case we must assume that step h may be neglected. We then have $\phi_{ISC} = \phi_t/\alpha$ for the combined yield of steps d and k. However, as shown above, if one is interested only in the activation energy of step d, the only assumption necessary for its calculation is that only this step is temperature dependent.

So far we have accepted the energy of activation as an experimental fact. It remains to ascribe it to a certain process. One possible explanation for the existence of such a potential barrier was forwarded recently by Borrell and Greenwood,[28] who made a SCF-CI analysis of the energies of the ground state and the four lowest excited states of stilbene as a function of the angle of twist around the central double bond. Their results are reproduced in Figure 14

(27) Unpublished results.

(28) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc.* (London), **A298**, 453 (1967).

(Figure 5 in the original paper). According to their picture, the molecule passes from the lowest excited singlet state, ^{1}B (*trans*), to the second triplet level ^{3}H, at the crossing point of the two curves, *i.e.*, *via* a slight twisting of the "double" bond. Passing from the initial state (x) to the crossover point (y) involves moving along a slightly rising curve, *i.e.*, overcoming a small barrier. This is followed by transition to the lowest triplet state, ^{3}B, and then crossover to the singlet ground state ^{1}A, *via* further twisting of the "double" bond toward the potential minimum of curve ^{3}B. It appears plausible that this potential minimum is identical with state X in our scheme (Figure 12), while our T_1 and T_1' are identical with ^{3}B in the *trans* and *cis* positions (0 and 180° twist, respectively); T_2 corresponds to ^{3}H, S_1 to ^{1}B, and S_0 to ^{1}A. In this picture the thermal energy which has to be supplied to ^{1}B is channelled into torsional energy (*i.e.*, moving from left to right in Figure 14). A second explanation for the existence of an activation energy is that T_2 is slightly above S_1 (Figure 12), and thermal energy is necessary to pass from S_1 to T_2, without involving a twist of the "double" bond during this stage. In either case the energies of S_1 and T_2 are close, and therefore relatively slight changes in them, as a result of substitution, may change the relative position of the two curves, on the left side, sufficiently to reduce this energy difference or even change its sign, and thus abolish the activation energy. In the *cis* isomers (the right side of Figure 14), all potential curves decline sharply during twisting (Borrell's picture), or else S_1 is in all cases above T_2.

Steric hindrance to coplanarity, introduced by substitution in the *ortho* positions of the rings or the α and β positions on the bridge (groups IV and V), is expected to make the situation on the *trans* side (Figure 14) more similar to that on the *cis* side by preventing coplanarity. The energies of the excited states will be raised, and thereby any plateau or shallow minimum will be eliminated. Alternatively, in such sterically hindered compounds the T_2 level might be raised less than the S_1 level and thereby fall below it. In a somewhat more quantitative way, the latter explanation may be expressed as follows. In the *trans* isomers of stilbenes in group IV, to some extent in α,β-dichlorostilbene, and in all *cis* isomers in their (hypothetical) planar configuration, the distance between groups at the *ortho* and α positions (and for some *cis* isomers the distance between the two groups at the nearest *ortho* positions) is smaller than the sum of the van der Waals radii of these groups. The resulting steric crowding is relieved chiefly by twisting about the 1–α single bonds, which requires the smallest energy and is sterically more effective than other deformation modes.[13,14] According to the FE–MO model of Jaffé and Orchin,[13] the effect of steric hindrance on ϕ_t may then be explained as follows. The main contribution to the lowest transition in stilbene is the promotion of an electron from the highest filled orbital ψ_7 (node at the 1–α bond) to the lowest unfilled orbital ψ_8 (node at the α–β bond). This transition moves to higher energies in sterically hindered stilbenes, as the bond order of the 1–α bond is increased in ψ_8, so that the energy of ψ_7 is lowered and the energy of ψ_8 is increased. The next transition involves orbitals with the opposite distribution of nodes, and its energy in sterically hindered stilbenes is lowered compared with the energy of this transition in stilbene.[13,29] The over-all result would be a compression of the excited levels and an increase in their energies.[13] Beveridge and Jaffé[30] have calculated the bond orders of the α–β bond in the lower excited triplet and singlet levels of *trans*-stilbene. Their result indicates that the bond order of a given bond is closely similar for a singlet and for a triplet level of the same configuration. Therefore one would expect a parallel effect of torsion around the 1–α bond on the triplet levels as on the singlet levels. As a result, level T_2 which lies 1-2 kcal/mole above level S_1 in *trans*-stilbene is expected to be lowered either below or very slightly above level S_1 in the sterically hindered stilbenes.

The SCF–CI calculations[28] provide an even more satisfactory qualitative explanation for the behavior found in compounds of this group. The T_2 level, into which intersystem crossing takes place, is identified with the $^3H^+$ state which has a major component of localized ring excitation.[28] Twisting about the 1–α bond would move both the S_1 state ^{1}B and the $^3H^+$ state to higher energies, but state $^3H^+$ would be much less influenced than state ^{1}B.

The absence of a potential barrier in 4-bromostilbene, and also in stilbene dissolved in butyl bromide,[3] may be due to a "heavy-atom effect," which through spin-orbit coupling between S_1 and T_1 enables a crossover $S_1 \rightarrow T_1$ (step k in our scheme), by-passing step d. This would also explain the small ϕ_F observed even at $-180°$. Alternatively, the heavy atom might change the relative positions of the S_1 and T_2 levels, putting S_1 above T_2. The reason for the absence of a temperature effect in the keto- and the nitro-substituted stilbenes (group II) may be similar. However, another reason may be the involvement of low-lying n–π^* levels supplied by the substituents. Here the π–π^* triplet level lies slightly *below* the first excited n–π^* singlet level,[23] thus allowing a $S_1 \rightarrow T_1$ transition.

Introduction of fluorine or chlorine in the 4 position in stilbene has practically no effect on the temperature dependence of ϕ_t. Together with the fact that ϕ_F is considerable in both derivatives, this indicates that the spin–orbit coupling introduced by these groups is insufficient to produce the effects observed in bromostilbene.

The difference between α,β-difluorostilbene and 4-fluorostilbene[7] regarding the dependence of ϕ_t on the temperature (slight in the former, strong in the latter) is probably the result of different π-electron densities at the heavy-atom-substituted positions in these molecules. The electron density at the α position (Hückel LCAO method) in the ψ_7 and ψ_8 orbitals is double that at the 4 position (0.192 *vs.* 0.098). Thus it is possible to account satisfactorily for the behavior observed in α,β-difluorostilbene if the intersystem crossing is taken here as an $S_1 \rightarrow T_1$ ($^1B \rightarrow {}^3B$) process. The lowest B states have a major contribution from the one-electron excitations (from ψ_7 to ψ_8).[28,30] In this respect α,β-dichlorostilbene is entirely similar. However, in this molecule a steric effect is superimposed on the heavy-atom effect, with both effects acting in the same direction.

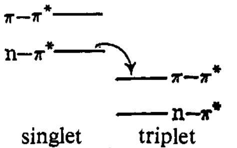
(29) R. I. T. Cromartie and J. N. Murrell, *J. Chem. Soc.*, 2063 (1961).

(30) D. L. Beveridge and H. H. Jaffé, *J. Am. Chem. Soc.*, **87**, 5340 (1965).

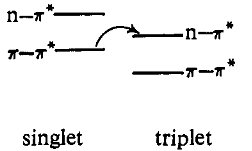
As to the actual positions of the triplet levels in stilbene, the energy of T_1 is known from the $S_0 \rightarrow T_1$ absorption.[7,31] The $T_1 \rightarrow T_n$ transitions have not been observed in flash photolysis experiments until very recently,[32] because of the short lifetime of T_1 caused by a very efficient radiationless decay.[11,26] Theoretical estimates of these levels have been made[30] by methods which are moderately successful in polycyclic aromatic hydrocarbons.[33,34]

The stilbenes in group III, 4-methoxy- and 4-dimethylamino-4′-nitrostilbene, are characterized by the pronounced solvent dependence of their emission spectra[12] (Figure 6) and their photoisomerization behavior.[11] This is clearly related to the high dipole moment of these molecules in their ground state[35] (5.6 and 7.6 D, respectively) and in particular in the first excited state (32 D for the second compound).[36] The solute–solvent interaction will therefore greatly increase with solvent polarity,[36] the effect being more pronounced in the dimethylamino derivative because this substituent is a much stronger electron donor than the methoxy group. Thus, 4-methoxy-4′-nitrostilbene in nonpolar solvents still behaves just like 4-nitrostilbene. Its fluorescence yield ϕ_F is very low, while its isomerization yield ϕ_t is high and temperature independent, both facts indicating efficient intersystem crossing. This is no longer so in alcoholic solutions of this compound ($\phi_F = 0.2$ at $-180°$, $\phi_t = 0.10$ as a high-temperature limiting value) and in all solutions of the dimethylaminonitro derivative. In both compounds the emission spectrum changes strongly with the temperature, besides depending on the solvent. ϕ_t in the second compound is practically zero in alcohols and changes sharply with the temperature in nonpolar solvents.

To explain these facts, we shall make use of the well-known hypsochromic shift of n–π^* bands, and the bathochromic shift of π–π^* bands, with increasing solvent polarity. Moreover, according to the selection rules of El-Sayed[22] for radiationless intersystem crossing, transitions between states of different configuration (*i.e.*, n–$\pi^* \rightleftarrows \pi$–$\pi^*$) are greatly preferred to those between states of similar configuration (*i.e.*, n–$\pi^* \rightleftarrows$ n–π^*, π–$\pi^* \rightleftarrows \pi$–$\pi^*$). Presumably in the methoxynitro derivative in nonpolar solvents the n–π^* levels are the lower ones, while this order is reversed in polar solvents. Intersystem crossing will thus proceed in the two types of solvents as depicted in the following scheme, where case B involves a slight barrier in the S → T crossover.



A

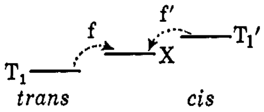


B

Regarding the nitrodimethylamino derivative, several additional factors have to be realized. The strong fluorescence in all solvents indicates that the lowest excited singlet level is a π–π^* one, and this is probably true also for the lowest triplet level (scheme B). The dipole moment of the *trans* isomer must be considerably larger than that of the *cis* isomer, because of the larger distance between the opposite charges. Therefore the energy gained by interaction with the medium according to the Onsager[37] equation

$$E = 2\mu^2(\epsilon - 1)/a^3(2\epsilon + 1)$$

(ϵ = dielectric constant, μ = dipole moment, a = radius of spheric cavity taken up by the solute) is much larger for the *trans* isomer. Passing from nonpolar to polar solvents results in a preferential stabilization of the excited *trans*, and thereby heightens the potential barrier for the *trans* → *cis* conversion in the excited state to such an extent that this conversion no longer takes place ($\phi_t \approx 0$). If this is so, the potential barrier for photoisomerization in this compound is on the way from excited *trans* to *cis*, *i.e.*, in steps f + g′, rather than in the intersystem crossing step d. We deduce that even in nonpolar solvents the X level is above T_1, and that the high activation energy of ϕ_t (5–10 kcal/mole) observed in these solvents is also due to a barrier in steps f + g′. In the more polarizable toluene the barrier is higher, again because the relative level of *trans* is lower. It appears more plausible that step f is to blame. Schematically we will then have



The preferential stabilization of the *trans* isomer by interaction with the medium will be further enhanced by the fact that the solvation of the planar *trans* isomer may be expected to be more effective than that of the distorted *cis* isomer.

The preferential stabilization of S_1, as compared with S_0, in solutions in polar solvents also explains[36] the observed red shift of the fluorescence of solutions in ethanol–methanol, as compared with those in MCH–IH (Figure 6b, c). In frozen alcohol, at $-180°$, the restricted motion of the solvent molecules prevents their redistribution around the excited solute molecule during the latter's lifetime. The red shift mentioned above is therefore less pronounced at $-180°$ than at $-130°$ (Figure 6c). A study of the solvent dependence of the sensitized photoisomerization of this compound (thus by-passing levels S_1 and T_2) promises to clarify the situation. It is hoped that an extension of calculations similar to those of Borrell and Greenwood[28] to substituted stilbenes will provide a more quantitative basis to the above ideas.

Experimental Section

All the techniques used have already been described in our earlier papers.[2–6,16] Stilbene, α,β-difluorostilbene, and azobenzene were commercial products. All other compounds were synthesized according to published methods.

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